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Reduction of CuO in H_2: *In Situ* Time-Resolved XRD Studies

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Beamline(s): X7B

Introduction: CuO is used as a catalyst or catalyst precursor in many chemical reactions that involve hydrogen as a reactant or product. It has been proposed that in several of these catalytic process CuO undergoes a complete reduction and metallic copper(Cu^0) is the real active phase [1]. For years, there has been controversy about the relative importance of Cu^{+1} and Cu^0 in centers in the methanol synthesis reaction [2,3]. In order to solve this issue one needs a fundamental understanding of the H_2 reaction with CuO [4].

Methods and Materials: Samples of CuO were loaded in a sapphire capillary attached to a flow-reaction cell similar to those described in refs. [5,6]. The sample was heated in the range of 150-300°C with a small resistance heater wrapped around the capillary. A 5%H_2/95%He mixture was flowed through the capillary and reactant gases where sampled with a SRS RGA. The XRD data were collected with a MAR345 image plate detector and the powder rings were integrated using FIT2D code [7].

Results: Fig. 1 shows typical results from the time resolved XRD and Fig. 2 shows H_2O formation determined from RGA.

Conclusions: Oxide reduction was observed but only after an induction period. High temperature or increased H_2 pressure lead to a decrease in the magnitude of the induction time. The H_2 flow rate determines the amount of Cu^{+1} formation. Under higher flow rates a direct CuO → Cu transformation occurs. To facilitate the generation of Cu^{+1} in a catalytic process one can limit the supply of H_2 or mix this molecule with molecules which can act as oxidizing agents (O_2, H_2O).

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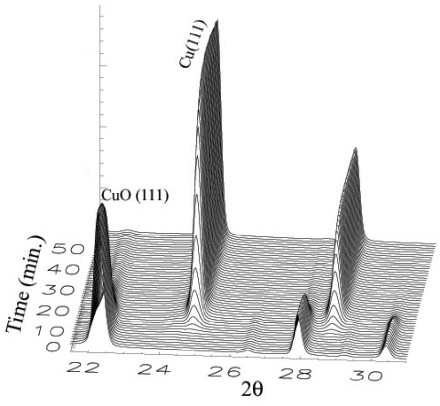

Fig1. In situ time-resolved XRD reduction of CuO to Cu^0. (flow rate 20cc/min)

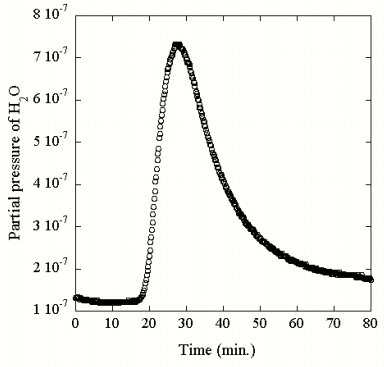

Fig. 2 Water formation during reduction in Fig. 1.